



US005399794A

United States Patent [19]

[11] **Patent Number:** **5,399,794**

Sanderson

[45] **Date of Patent:** **Mar. 21, 1995**

[54] **USE OF SUPPORTED PALLADIUM/GOLD CATALYSTS IN THE PREPARATION OF TERTIARY BUTYL ALCOHOL FROM TERTIARY BUTYL HYDROPEROXIDE**

Attorney, Agent, or Firm—Kenneth R. Priem; James L. Bailey; Carl G. Ries

[75] **Inventor:** **John R. Sanderson**, Leander, Tex.

[57] **ABSTRACT**

[73] **Assignee:** **Texaco Chemical Inc.**, White Plains, N.Y.

A method for preparing tertiary butyl alcohol wherein a feedstock comprising a solvent solution of tertiary butyl hydroperoxide in tertiary butyl alcohol or a mixture of tertiary butyl alcohol with isobutane is charged to a hydroperoxide decomposition reaction zone containing a catalytically effective amount of a hydroperoxide decomposition catalyst consisting essentially of alumina having gold-promoted palladium deposited thereon and is brought into contact with the catalyst in liquid phase with agitation under hydroperoxide decomposition reaction conditions to convert the tertiary butyl hydroperoxide to decomposition products, principally tertiary butyl alcohol.

[21] **Appl. No.:** **150,912**

[22] **Filed:** **Nov. 12, 1993**

[51] **Int. Cl.⁶** **C07C 29/132; C07C 31/12**

[52] **U.S. Cl.** **568/909.8; 568/385; 568/922**

[58] **Field of Search** **568/909.8**

Primary Examiner—Joseph E. Evans

7 Claims, No Drawings

USE OF SUPPORTED PALLADIUM/GOLD CATALYSTS IN THE PREPARATION OF TERTIARY BUTYL ALCOHOL FROM TERTIARY BUTYL HYDROPEROXIDE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the catalytic decomposition of tertiary butyl hydroperoxide (TBHP). More particularly, this invention relates to a method for the preparation of tertiary butyl alcohol (TBA) by the catalytic decomposition of tertiary butyl hydroperoxide. Still more particularly, this invention relates to a method wherein an alumina supported palladium/gold catalyst is used to catalyze the substantially selective decomposition of tertiary butyl hydroperoxide to tertiary butyl alcohol.

2. Prior Art

It is known to react isobutane with oxygen, either thermally or catalytically, to form a peroxidation reaction product wherein the principal peroxide that is formed is tertiary butyl hydroperoxide. It is also known to thermally or catalytically decompose the tertiary butyl hydroperoxide to form tertiary butyl alcohol.

In the text entitled "Organic Peroxides" edited by Daniel Swern (Wiley Interscience, a Division of John Wiley & Sons, New York), in Vol. II on page 157 it is stated that the metal-ion-catalyzed decomposition of primary hydroperoxides yields mainly alcohols, aldehydes and carboxylic acids, citing as an example the decomposition of hydroxymethylhydroperoxide with aqueous ferrous sulfate to provide formaldehyde, formic acid and water.

Quin U.S. Pat. No. 2,854,487 discloses the hydrogenation of hydrocarbon peroxides in the presence of hydrogen and palladium on activated alumina to provide carbinols.

In Massie U.S. Pat. No. 3,775,472 a process is disclosed wherein alkyl substituted aromatic hydrocarbons are oxidized to products such as aromatic alcohols, aldehydes and carboxylic acids in the presence of ruthenium compounds.

Grane U.S. Pat. No. 3,474,151 discloses that tertiary butyl alcohol starts to dehydrate at 450° F. and to decompose at a "rapid rate" at temperatures above 475° F. Grane discovered, however, that residual quantities of hydroperoxide contaminants present in tertiary butyl alcohol could be thermally decomposed by heating the contaminated tertiary butyl alcohol at a temperature of 375° to 475° F. for about 1 to 10 minutes.

Grane et al. U.S. Pat. No. 4,294,999 discloses a process wherein isobutane is oxidized in a pressured reactor in the presence of a solubilized molybdenum catalyst to provide a mixture of tertiary butyl alcohol, tertiary butyl hydroperoxide, methanol, acetone, and other oxygen-containing compounds. The tertiary butyl hydroperoxide is thermally decomposed under pressure at about 280° F. to provide a tertiary butyl alcohol product containing only residual quantities of tertiary butyl hydroperoxide which are then decomposed in accordance with Grane U.S. Pat. No. 3,474,151 by heating the tertiary butyl alcohol at 375° to 475° for about 1 to 10 minutes. Heating tertiary butyl alcohol containing small amounts of peroxides at high temperatures for even short periods of time to remove the peroxides produces undesirable products such as isobutylene.

Grane et al. U.S. Pat. No. 4,296,262 discloses a related process wherein isobutane is reacted with oxygen in a reaction zone for a residence time of about 1 to 10 hours at a temperature of about 240° to about 340° F. and a pressure of about 100 to about 1000 psig. in the presence of a catalytically effective amount of a soluble molybdenum catalyst. A liquid stream comprising tertiary butyl alcohol is recovered from the reaction mixture and fed to a decomposition zone wherein the tertiary butyl hydroperoxide contained therein is decomposed by "hot aging" at 250°-350° F. at a pressure lower than the pressure in the oxidation zone. The tertiary butyl alcohol can be further subjected to a clean-up treatment at 375°-475° F. for 1 to 10 minutes. Worrell et al. in U.S. Pat. No. 4,296,263 disclose a related process wherein the feedstock is a mixture of normal butane with isobutane and wherein the oxidation catalyst is a soluble form of chromium, cobalt, nickel, manganese, molybdenum, or a mixture thereof.

In U.S. Pat. No. 3,505,360, Allison et al. disclose a method wherein an alkenyl hydroperoxide is decomposed in the presence of a catalyst based on a compound of a Group IV-A, V-A or VI-A metal. Taylor et al., in U.S. Pat. No. 4,508,923 disclose the use of a catalyst system comprising ruthenium and chromium for decomposing organic hydroperoxides. The use of a cobalt borate catalyst for the decomposition of hydroperoxides is disclosed in Sanderson et al. U.S. Pat. No. 4,547,598.

Taylor et al. U.S. Pat. No. 4,551,553 is directed to a process for the formation of alcohols such as tertiary butyl alcohol by the catalytic decomposition of an organic hydroperoxide such as tertiary butyl hydroperoxide using a binary catalyst composed of a mixture of a ruthenium compound with a chromium compound. It is stated that the use of the binary catalyst eliminates the need for stabilizing ligands.

Sanderson et al. disclose the use of a variety of catalysts for the decomposition of tertiary butyl hydroperoxide in a series of U.S. patents, including a catalyst composed of unsupported nickel, copper, chromia and iron (U.S. Pat. No. 4,704,482), a catalyst composed of iron, copper, chromia and cobalt (U.S. Pat. No. 4,705,903), a catalyst composed of a base treated hydrogenation catalyst from groups VIB or VIIB of the Periodic Table (U.S. Pat. No. 4,742,179), a catalyst consisting essentially of nickel, copper, chromium and barium (U.S. Pat. No. 4,873,380), a catalyst composed of a metal phthalocyanine promoted with a rhenium compound (U.S. Pat. No. 4,910,349), a catalyst composed of a base promoted metal phthalocyanine compound (U.S. Pat. No. 4,912,269), a catalyst composed of a soluble ruthenium compound promoted with a bidentate ligand (U.S. Pat. No. 4,912,033), a catalyst composed of a metal porphine such as iron (III) or manganese (III) promoted with an alkyl thiol or an amine, a catalyst composed of an imidazole promoted metal phthalocyanine compound (U.S. Pat. No. 4,912,266), (U.S. Pat. No. 4,922,034), a catalyst composed of a metal phthalocyanine promoted with a thiol and a free radical inhibitor (U.S. Pat. No. 4,922,035), a catalyst composed of a borate promoted metal phthalocyanine (U.S. Pat. No. 4,922,036), or a catalyst composed of a soluble ruthenium compound and an iron compound such as an acetate, a borate, a bromide, a chloride, a 1,3-propanedionate, a 2-ethyl-hexanoate, an iodide, a nitrate, a 2,4-pentanedionate, a perchlorate or a sulfate (U.S. Pat. No. 5,025,113).

BACKGROUND INFORMATION

When isobutane is reacted with molecular oxygen, the principal products of the reaction are tertiary butyl alcohol and tertiary butyl hydroperoxide. However, minor amounts of other contaminants are also formed.

In addition, a minor amount of water will be formed, which will normally amount to about 0.5 to 1 wt. % of the reactor effluent. The amount of byproduct water that is produced is a function of the severity of the reaction conditions employed and will tend to increase as the severity of the reaction conditions is increased.

As indicated, tertiary butyl hydroperoxide is useful as a raw material for the manufacture of tertiary butyl alcohol. The tertiary butyl alcohol can be formed by catalytic decomposition of the tertiary butyl hydroperoxide. In the Williams et al. process disclosed in U.S. Pat. No. 3,472,876, an oxygen-containing gas was charged to a reactor containing isobutane and an oxidation catalyst to provide a reaction mixture comprising tertiary butyl alcohol, tertiary butyl hydroperoxide, acetone, and tertiary butyl ether. The reported results in the patent indicate that there was a comparatively low rate of conversion and a comparatively poor selectivity of the reaction to tertiary butyl alcohol.

SUMMARY OF THE INVENTION

In accordance with the present invention, a solvent solution of a tertiary butyl hydroperoxide charge stock is brought into contact with a catalytically effective amount of a hydroperoxide decomposition catalyst in a hydroperoxide decomposition reaction zone in liquid phase with agitation to convert the tertiary butyl hydroperoxide to decomposition products, principally tertiary butyl alcohol, the hydroperoxide decomposition catalyst being a supported hydroperoxide decomposition catalyst consisting essentially of alumina having deposited thereon from about 0.1 to about 1 wt. % of a mixture of palladium and gold in the ratio of about 0.01 to about 1 part of gold per part of palladium, and tertiary butyl alcohol is recovered from the products of the hydroperoxide decomposition reaction.

In accordance with a preferred embodiment of the present invention, the hydroperoxide decomposition catalyst is diluted with titania or zirconia.

The tertiary butyl alcohol will not be the only decomposition product that is formed. Minor amounts of other oxygen-containing materials such as those listed above will also be formed.

The tertiary butyl alcohol that is recovered from the decomposition reaction mixture will be contaminated with the oxygenated impurities.

DESCRIPTION OF THE PROCESS OF THE PRESENT INVENTION

The starting materials for the process of the present invention are a tertiary butyl hydroperoxide feedstock and a supported palladium/gold catalyst.

The Tertiary Butyl Hydroperoxide Feedstock

The tertiary butyl hydroperoxide charge stock may comprise an isobutane oxidation product wherein the tertiary butyl hydroperoxide is dissolved in a mixture of isobutane and tertiary butyl alcohol or may comprise an isobutane oxidation product enriched by the addition of tertiary butyl alcohol, such that the solution of tertiary butyl alcohol in the mixture of isobutane with tertiary butyl alcohol contains from about 5 to about 30 wt. %

of tertiary butyl hydroperoxide. A surprising and unexpected increase in the yield of tertiary butyl alcohol is obtained with a feedstock comprising tertiary butyl hydroperoxide dissolved in a solvent mixture of isobutane with tertiary butyl alcohol.

The isobutane reaction product may be charged to a distillation zone where unreacted isobutane is removed as a distillate fraction for recycle to thereby provide a solution of tertiary butyl hydroperoxide in tertiary butyl alcohol containing about 5 to about 30 wt. % of tertiary butyl hydroperoxide.

The Catalyst System

The hydroperoxide decomposition catalyst to be used in accordance with the present invention is a supported hydroperoxide decomposition catalyst consisting essentially of alumina having deposited thereon from about 0.1 to about 1 wt. % of a mixture of palladium and gold in the ratio of about 0.01 to about 1 part of gold per part of palladium, and tertiary butyl alcohol is recovered from the products of the hydroperoxide decomposition reaction.

In accordance with a preferred embodiment of the present invention, the hydroperoxide decomposition catalyst is diluted with from about 100 to about 500 wt. % of titania or zirconia, based on the weight of the alumina.

Catalytic Decomposition of Tertiary Butyl Hydroperoxide

The process of the present invention may be conducted batchwise in kettles or by continuously passing the reactants through a tubular reactor.

The catalytic decomposition of the tertiary butyl hydroperoxide is preferably conducted at a temperature within the range of about 20° to about 160° C. and, more preferably, at a temperature within the range of about 60° to about 120° C., and still more preferably at a temperature of about 80° to 100° C. The reaction is preferably conducted at a pressure sufficient to keep products and reactants in liquid phase, such as a pressure of about 0 to about 10,000 psig. may be used, if desired.

Flow rates of the charge solution to the reaction zone should be adjusted in order to provide an appropriate contact time within the reactor. In a batch process, the holding time may suitably be from about 0.5 to about 10 hours, and more preferably about 1 to 3 hours.

In accordance with the most preferred embodiment of the present invention, isobutane is reacted with oxygen in an oxidation zone under oxidation reaction conditions including a temperature of about 135° to about 155° C., a pressure of about 300 to about 800 psig., and a holding time of about 2 to about 6 hours to provide an initial oxidation reaction product comprising unreacted isobutane, tertiary butyl hydroperoxide, tertiary butyl alcohol, and oxygen-containing by-products. The initial oxidation reaction product is then used as the tertiary butyl hydroperoxide charge stock of the present invention. If the concentration of tertiary butyl hydroperoxide in the tertiary butyl hydroperoxide charge stock is more than about 30 wt. % of the initial oxidation reaction product, the initial oxidation reaction product can be diluted with an amount of tertiary butyl alcohol sufficient to lower the concentration of the tertiary butyl hydroperoxide to a desired percentage, to provide, for example, a tertiary butyl hydroperoxide charge stock containing from about 15 to about 25 wt. % of tertiary butyl hydroperoxide.

Alternately, the initial oxidation reaction product may be fractionated in any appropriate manner (e.g., by distillation in a distillation zone) to remove the isobutane therefrom for recycle and to provide a solution of tertiary butyl hydroperoxide and tertiary butyl alcohol which will normally contain from about 5 to about 30 wt. % of tertiary butyl hydroperoxide.

The solution of tertiary butyl hydroperoxide in tertiary butyl alcohol is then charged to a catalytic hydroperoxide decomposition zone where it is brought into contact with an alumina supported palladium/gold catalyst to substantially selectively convert the tertiary butyl hydroperoxide to tertiary butyl alcohol with high yields and selectivities.

As indicated, the catalytic decomposition of the tertiary butyl hydroperoxide in the catalytic hydroperoxide decomposition reaction zone may suitably be conducted at a temperature within the range of about 20° to about 160° C., preferably from about 60° to about 120° C., and more preferably from about 80° to 100° C. at autogeneous pressure or if desired at a super-atmospheric pressure up to 1000 psig. for a contact time within the range of about 0.5 to about 10 hours, and more preferably about 1 to 3 hours.

When the process of the present invention is practiced in a continuous manner by continuously charging the tertiary butyl hydroperoxide charge stock to a reactor containing a fixed bed of pelleted hydroperoxide decomposition catalyst, the space velocity is suitably in the range of about 0.5 to about 3 volumes of tertiary

butyl hydroperoxide charge stock per volume of catalyst per hour. Preferably, the space velocity is within the range of about 1 to about 2 volumes of tertiary butyl hydroperoxide charge stock per volume of catalyst per hour.

The reaction product from the tertiary butyl hydroperoxide decomposition step may then be fractionated in any suitable manner, such as by distillation to recover the tertiary butyl alcohol.

SPECIFIC EXAMPLES

The invention will be further illustrated by the following specific examples which are given by way of illustration and not as limitations on the scope of this invention.

The reactor was a stainless steel tube (0.51"×29") which was electrically heated. Liquid feed was pumped into the bottom of the reactor. Pressure regulation was with a Skinner Uni-Flow valve and a Foxboro controller. The liquid feed was pumped with a Ruska dual drive pump.

20% TBHP was prepared from 55% isobutane peroxidation reactor effluent by diluting with commercial TBA.

Analysis of the reactor effluent was by GC. Details are given in the following tables.

EXAMPLE 1

In this example, the catalyst consisted essentially of gold-promoted palladium supported on alumina.

TABLE 1
CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE TO TERT-BUTYLALCOHOL

Notebook Number	7012-25-F	7012-25-1	7012-25-2	7012-25-3	7012-25-4
Catalyst	(2% Pd, .08% Au on Al ₂ O ₃)				
Catalyst (cc)	100	100	100	100	100
Pressure (psig)	300	300	300	300	300
Feed Rate (cc/Hr.)	50	50	50	50	50
Temperature (°C.)	40	60	80	80	100
Time on Stream (Hr)	4	4	4	4	4
Space Vel. (cc/cc)	0.5	0.5	0.5	0.5	0.5
TBHP ¹ Conversion (mol. %)	56.3	82.7	92.9	99.6	99.6
IB ² Conversion (mol. %)	13.1	0.0	13.4	3.5	3.5
Sel. Acetone (mol. %)	0.2	2.3	6.9	6.8	6.8
Sel. Methanol (mol. %)	0.0	0.2	0.7	0.5	0.5
Sel. TBA ³ (mol. %)	99.8	91.7	86.9	89.5	89.5
Sel. DTBP ⁴ (mol. %)	0.0	6.1	6.1	3.7	3.7
<u>Composition, wt %</u>					
C3=	0.019	0.020	0.023	0.029	0.029
Isobutane	57.704	50.167	58.187	49.961	55.712
MEOH ⁵ /MF ⁶	0.101	0.089	0.112	0.142	0.136
Acetone	1.128	1.139	1.346	1.875	1.915
TBA	21.338	38.448	34.791	43.904	40.044
DTBP	0.681	0.404	1.418	1.518	1.220
TBHP	18.084	7.894	3.126	1.291	0.079

¹Tertiary butyl hydroperoxide

²Isobutane

³Tertiary butyl alcohol

⁴Ditertiary butyl peroxide

⁵Methanol

⁶Methyl formate

TABLE 2

CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE TO TERT-BUTYLALCOHOL

Notebook Number	7012-25-F	7012-25-5	7012-25-6	7012-25-7	7012-25-8
Catalyst	(2% Pd, .08% Au on Al ₂ O ₃)				
Catalyst (cc)	100	100	100	100	100
Pressure (psig)	300	300	300	300	300
Feed Rate (cc/Hr.)	50	50	so	50	50
Temperature (°C.)	40	60	so	100	100
Time on Stream (Hr)	4	4	4	4	4
Spact Vel. (cc/cc)	0.5	0.5	0.5	0.5	0.5

TABLE 2-continued

CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE TO TERT-BUTYLALCOHOL					
Notebook Number	7012-25-F	7012-25-5	7012-25-6	7012-25-7	7012-25-8
TBHP ¹ Conversion (mol. %)		21.7	62.9	87.8	96.5
IB ² Conversion (mol. %)		1.2	n.d.	0.3	7.5
Sel. Acetone (mol. %)		2.5	1.9	4.7	7.6
Sel. Methanol (mol. %)		0.5	0.2	0.5	1.0
Sel. TBA ³ (mol. %)		88.4	92.1	90.6	88.1
Sel. DTBP ⁴ (mol. %)		9.1	6.0	4.7	4.3
<u>Composition, wt %</u>					
Isobutane	57.704	56.992	59.018	57.534	53.360
MEOH ⁵ /MF ⁶	0.101	0.108	0.110	0.131	0.163
Acetone	1.128	1.191	1.265	1.605	1.988
TBA	21.338	25.640	30.712	36.183	41.556
DTBP	0.681	0.971	1.237	1.291	1.285
TBHP	18.084	14.165	6.709	2.198	0.631

¹Tertiary butyl hydroperoxide²Isobutane³Tertiary butyl alcohol⁴Ditertiary butyl peroxide⁵Methanol⁶Methyl formate

TABLE 3

CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE TO TERT-BUTYLALCOHOL					
Notebook Number	7012-25-F	7012-26-1	7012-26-2	7012-26-3	7012-26-4
Catalyst	(2% Pd, .08% Au on Al ₂ O ₃)				
Catalyst (cc)	100	100	100	100	100
Pressure (psig)	300	300	300	300	300
Feed Rate (cc/Hr.)	100	100	100	100	100
Temperature (°C.)	40	60	80	100	100
Time on Stream (Hr)	4	4	4	4	4
Space Vel. (cc/cc)	1.0	1.0	1.0	1.0	1.0
TBHP ¹ Conversion (mol. %)	4.9	56.0	83.2	95.7	95.7
IB ² Conversion (mol. %)	n.d.	n.d.	11.0	12.9	12.9
Sel. Acetone (mol. %)	n.d.	1.6	6.9	11.3	11.3
Sel. Methanol (mol. %)	n.d.	0.1	4.7	6.1	6.1
Sel. TBA ³ (mol. %)	n.d.	93.0	88.0	85.2	85.2
Sel. DTBA ⁴ (mol. %)	n.d.	5.4	5.0	3.5	3.5
<u>Composition, wt %</u>					
Isobutane	57.704	58.610	60.017	51.337	50.249
MEOH ⁵ /MF ⁶	0.101	0.099	0.106	0.351	0.477
Acetone	1.128	1.077	1.232	1.801	2.386
TBA	21.338	21.354	28.601	40.571	43.475
DTBP	0.681	0.714	1.121	1.292	1.172
TBHP	18.084	17.198	7.959	3.039	0.773

¹Tertiary butyl hydroperoxide²Isobutane³Tertiary butyl alcohol⁴Ditertiary butyl peroxide⁵Methanol⁶Methyl formate

TABLE 4

CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE TO TERT-BUTYLALCOHOL					
Notebook Number	7012-25-F	7012-27-1	7012-27-2	7012-27-3	7012-27-4
Catalyst	(2% Pd, .08% Au on Al ₂ O ₃)				
Catalyst (cc)	100	100	100	100	100
Pressure (psig)	300	300	300	300	300
Feed Rate (cc/Hr.)	200	200	200	200	200
Temperature (°C.)	40	60	80	100	100
Time on Stream (Hr)	4	4	4	4	4
Space Vel. (cc/cc)	2.0	2.0	2.0	2.0	2.0
TBHP ¹ Conversion (mol. %)	0.0	22.6	67.9	92.4	92.4
IB ² Conversion (mol. %)	7.8	6.1	16.7	16.9	16.9
Sel. Acetone (mol. %)	n.d.	5.2	9.1	15.7	15.7
Sel. Methanol (mol. %)	n.d.	1.3	1.4	2.9	2.9
Sel. TBA ³ (mol. %)	n.d.	84.1	83.2	79.5	79.5
Sel. DTBP ⁴ (mol. %)	n.d.	10.7	7.7	4.8	4.8
<u>Composition, wt %</u>					
Isobutane	57.704	53.231	54.157	48.039	47.959
MEOH ⁵ /MF ⁶	0.101	0.114	0.120	0.163	0.273
Acetone	1.128	1.223	1.264	1.849	2.821
TBA	21.338	24.306	28.374	41.215	44.881
DTBP	0.681	0.793	1.036	1.443	1.327

TABLE 4-continued

CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE TO TERT-BUTYLALCOHOL					
Notebook Number	7012-25-F	7012-27-1	7012-27-2	7012-27-3	7012-27-4
TBHP	18.084	19.310	13.996	5.799	1.383

¹Tertiary butyl hydroperoxide²Isobutane³Tertiary butyl alcohol⁴Ditertiary butyl peroxide⁵Methanol⁶Methyl formate

It will be noted from Tables 1-4 that conversion of the tertiary butyl hydroperoxide was consistently in excess of 90% only at a temperature of about 100° C. The selectivity to TBA is somewhat higher in the presence of IB. We believe that at least a portion of the IB is converted to TBA. The selectivity to TBA is consistently higher at lower temperatures and drops off at higher temperatures. The selectivity to DTBP is also higher at lower temperatures. The DTBP can be isolated for sale by a number of methods (see, for example, U.S. Pat. No. 4,810,809) or it may be converted to additional TBA by any of the methods disclosed in the prior art. The selectivity to the lower value by-products acetone and methanol are higher at higher temperatures.

One must choose between a conversion and selectivity which is most economical.

EXAMPLE 2

In Example 2, the catalyst was composed of 20 wt. % of the alumina-supported, gold promoted palladium catalyst of Example 1 diluted with 80 wt. % of titania.

Note from Tables 5-7 that with only 20 wt. % of the catalyst of Example 1, the conversion of tertiary butyl hydroperoxide was about 90% of the conversion obtained in Example 1. This is especially significant since Pd and Au catalysts are quite expensive. The "dilution" of the Pd/Au catalyst with the more economical TiO₂ gave a catalyst which is almost as reactive as the Pd/Au catalyst alone. Conversion/selectivity remains high.

TABLE 5

CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE TO TERT-BUTYLALCOHOL						
Notebook No.	7012-51-F1, F2	7012-51-1	7012-51-2	7012-51-3	7012-51-4	7012-51-5
Catalyst	20 cc (.2% Pd, .08% Au on Al ₂ O ₃) 80 cc Titania					
Catalyst (cc)	100	100	100	100	100	100
Pressure (psig)	300	300	300	300	300	300
Feed Rate (cc/H)	50	50	50	50	50	50
Temperature (°C.)	60	70	80	80	90	100
Time on Stream (Hr)	4	4	4	4	4	4
Space Vel. (cc/cc)	0.5	0.5	0.5	0.5	0.5	0.5
TBHP Conversion (mol. %)	32.7	75.8	82.0	82.9	82.9	87.0
IB Conversion (mol. %)	26.0	5.0	3.8	4.4	15.8	15.8
Sel. Acetone (mol. %)	12.0	4.3	4.8	8.0	10.4	10.4
Sel. Methanol (mol. %)	2.2	0.7	1.1	1.1	1.8	1.8
Sel. TBA (mol. %)	62.8	89.8	89.8	87.0	82.5	82.5
Sel. DTBP (mol. %)	25.2	5.8	5.4	5.1	7.1	7.1
Remarks	H ₂ O Free Basis	H ₂ O Free Basis	H ₂ O Free Basis	H ₂ O Free Basis	H ₂ O Free Basis	H ₂ O Free Basis
<u>Composition, wt. %</u>						
Isobutane	70.468	52.139	66.941	67.785	67.359	59.351
MEOH/MF	0.103	0.138	0.130	0.146	0.148	0.179
Acetone	0.930	1.285	1.226	1.283	1.525	1.742
TBA	13.739	35.002	26.889	26.811	27.018	34.924
DTBP	0.267	1.202	0.768	0.770	0.744	0.970
TBHP	13.980	9.402	3.388	2.522	2.388	1.814

TABLE 6

CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE TO TERT-BUTYLALCOHOL						
Notebook No.	7012-51-F1, F2	7012-52-1	7012-52-2	7012-52-3	7012-52-4	7012-52-5
Catalyst	20 cc (.2% Pd, .08% Au on Al ₂ O ₃) 80 cc Titania					
Catalyst (cc)	100	100	100	100	100	100
Pressure (psig)	300	300	300	300	300	300
Feed Rate (cc/H)	100	100	100	100	100	100
Temperature (°C.)	60	70	80	90	100	100
Time on Stream (Hr)	4	4	4	4	4	4
Space Vel. (cc/cc)	1.0	1.0	1.0	1.0	1.0	1.0
TBHP Conversion (mol. %)	19.8	41.8	29.0	45.7	84.7	84.7
IB Conversion (mol. %)	1.4	2.5	3.7	6.1	11.6	11.6
Sel. Acetone (mol. %)	3.8	3.5	4.9	6.1	10.3	10.3
Sel. Methanol (mol. %)	1.0	0.7	1.5	1.5	2.2	2.2
Sel. TBA (mol. %)	89.5	90.6	89.2	88.5	85.4	85.4

TABLE 6-continued

CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE TO TERT-BUTYLALCOHOL						
Notebook No.	7012-51-F1, F2	7012-52-1	7012-52-2	7012-52-3	7012-52-4	7012-52-5
Sel. DTBP (mol. %)		6.7	6.0	5.9	5.4	4.3
Remarks		H ₂ O Free Basis				
<u>Composition, wt. %</u>						
Isobutane	70.468	69.484	68.722	67.844	66.195	62.267
MEOH/MF	0.103	0.113	0.118	0.124	0.136	0.195
Acetone	0.930	0.998	1.061	1.058	1.182	1.715
TBA	13.739	17.240	20.826	19.989	23.660	32.117
DTBP	0.267	0.418	0.549	0.461	0.545	0.684
TBHP	13.980	11.209	8.138	9.919	7.590	2.140

TABLE 7

CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE TO TERT-BUTYLALCOHOL						
Notebook No.	7012-51-F1, F2	7012-53-1	7012-53-2	7012-53-3	7012-53-4	7012-53-5
Catalyst	20 cc (.2% Pd, .08% Au on Al ₂ O ₃) 80 cc Titania					
Catalyst (cc)	100	100	100	100	100	100
Pressure (psig)	300	300	300	300	300	300
Feed Rate (cc/H)	200	200	200	200	200	200
Temperature (°C.)	60	70	80	90	100	100
Time on Stream (Hr)	4	4	4	4	4	4
Space Vel. (cc/cc)	2.0	2.0	2.0	2.0	2.0	2.0
TBHP Conversion (mol. %)	8.4	15.4	42.1	76.3	81.8	81.8
IB Conversion (mol. %)	4.2	6.1	15.3	2.0	7.4	7.4
Sel. Acetone (mol. %)	n.d.	8.2	9.6	5.4	9.1	9.1
Sel. Methanol (mol. %)	n.d.	2.6	2.5	1.1	2.0	2.0
Sel. TBA (mol. %)	n.d.	80.9	81.2	90.7	87.2	87.2
Sel. DTBP (mol. %)	n.d.	10.8	9.2	3.8	3.7	3.7
Remarks		H ₂ O Free Basis				
<u>Composition, wt. %</u>						
Isobutane	70.468	67.530	66.195	59.662	69.050	65.266
MEOH/MF	0.103	0.120	0.123	0.155	0.146	0.185
Acetone	0.930	1.012	1.044	1.294	1.304	1.602
TBA	13.739	17.576	19.717	29.274	24.863	28.934
DTBP	0.267	0.383	0.455	0.706	0.600	0.611
TBHP	13.980	12.811	11.834	8.100	3.308	2.541

EXAMPLE 3

In Example 3, the catalyst was composed of 20 wt. % of the alumina-supported, gold promoted palladium 45 catalyst of Example 1 diluted with 80 wt. % of zirconia.

Note from Tables 8 and 9 that with only 20 wt. % of the catalyst of Example 1, the conversion of tertiary

butyl hydroperoxide was about 95% of the conversion obtained in Example 1. Again, the dilution of the more expensive Pd/Au catalyst with ZrO₂ gave a catalyst which was almost as active as the Pd/Au catalyst alone. There was not a significant conversion/selectivity loss to desired products.

TABLE 8

CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE TO TERT-BUTYLALCOHOL						
Notebook No.	7082-7-F1, F2	7082-22-1	7082-22-2	7082-22-3	7082-22-4	7082-22-5
Catalyst	20 cc (.2% Pd, .08% Au on Al ₂ O ₃) 80 cc Zirconia					
Catalyst (cc)	100	100	100	100	100	100
Pressure (psig)	300	300	300	300	300	300
Feed Rate (cc/H)	100	100	100	100	100	100
Temperature (°C.)	60	70	80	90	100	100
Time on Stream (Hr)	4	4	4	4	4	4
Space Vel. (cc/cc)	1.0	1.0	1.0	1.0	1.0	1.0
TBHP Conversion (mol. %)	35.1	56.4	79.5	87.8	94.1	94.1
IB Conversion (mol. %)	3.8	4.3	4.9	5.1	7.1	7.1
Sel. Acetone (mol. %)	6.8	5.2	6.7	9.5	15.1	15.1
Sel. Methanol (mol. %)	1.5	0.9	0.9	1.2	2.0	2.0
Sel. TBA (mol. %)	85.9	88.3	88.3	86.2	81.2	81.2
Sel. DTBP (mol. %)	7.3	6.5	5.0	4.3	3.8	3.8
Remarks		H ₂ O Free Basis				
<u>Composition, wt. %</u>						
Isobutane	71.310	68.580	68.244	67.822	67.639	66.243

TABLE 8-continued

CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE TO TERT-BUTYLALCOHOL						
Notebook No.	7082-7-F1, F2	7082-22-1	7082-22-2	7082-22-3	7082-22-4	7082-22-5
MEOH/MF	0.151	0.177	0.176	0.186	0.202	0.240
Acetone	0.844	1.052	1.102	1.307	1.574	2.085
TBA	13.137	20.249	23.195	26.448	27.535	29.229
DTBP	0.259	0.542	0.663	0.699	0.673	0.649
TBHP	13.568	8.804	5.919	2.777	1.652	0.795

TABLE 9

CATALYTIC CONVERSION OF TERT-BUTYLHYDROPEROXIDE TO TERT-BUTYLALCOHOL						
Notebook No.	7082-7-F1, F2	7082-23-1	7082-23-2	7082-23-3	7082-23-4	7082-23-5
Catalyst	20 cc (.2% Pd, .08% Au on Al ₂ O ₃) 80 cc Zirconia					
Catalyst (cc)	100	100	100	100	100	100
Pressure (psig)	300	300	300	300	300	300
Feed Rate (cc/H)	200	200	200	200	200	200
Temperature (°C.)	60	70	80	90	100	100
Time on Stream (Hr)	4	4	4	4	4	4
Space Vel. (cc/cc)	2.0	2.0	2.0	2.0	2.0	2.0
TBHP Conversion (mol. %)	7.8	45.8	79.5	86.7	91.3	91.3
IB Conversion (mol. %)	4.7	2.7	5.0	7.5	7.4	7.4
Sel. Acetone (mol. %)	n.d.	5.4	7.2	11.3	15.6	15.6
Sel. Methanol (mol. %)	n.d.	1.2	1.1	1.9	2.5	2.5
Sel. TBA (mol. %)	n.d.	88.7	87.9	84.5	80.7	80.7
Sel. DTBP (mol. %)	n.d.	5.9	4.9	4.2	3.6	3.6
Remarks	H ₂ O Free Basis	H ₂ O Free Basis	H ₂ O Free Basis	H ₂ O Free Basis	H ₂ O Free Basis	H ₂ O Free Basis
Composition, wt. %						
Isobutane	71.310	67.970	69.353	67.709	65.993	66.016
MEOH/MF	0.151	0.177	0.178	0.194	0.232	0.262
Acetone	0.844	0.988	1.061	1.346	1.703	2.093
TBA	13.137	17.322	20.848	26.535	28.882	29.020
DTBP	0.259	0.407	0.557	0.687	0.657	0.623
TBHP	13.568	12.515	7.359	2.781	1.811	1.182

Comparative Example

In Table 10, the catalyst was composed of 0.8 wt. % of palladium supported on alumina. Note that there was a significantly lower selectivity of the tertiary butyl hydroperoxide to tertiary butyl alcohol.

In Table 11, the tertiary butyl hydroperoxide charge stock was passed over pelleted titania. Note that there was a significantly lower selectivity of the tertiary butyl hydroperoxide to tertiary butyl alcohol.

In Table 12, the tertiary butyl hydroperoxide charge stock was passed over pelleted zirconia. Again, note that there was a significantly lower selectivity of the tertiary butyl hydroperoxide to tertiary butyl alcohol.

It is surprising that the "dilution" of our active catalyst such as the Pd/Au catalyst with a poor-fair catalyst such as the ZrO₂ or TiO₂ catalysts disclosed would lead to a catalyst mixture which is almost as active as the Pd/Au catalyst alone. This system has the added advantage that it is much more economical.

TABLE 10

CATALYTIC CONVERSION OF TBHP TO TBA (CONTINUOUS REACTOR)								
Notebook Number	Catalyst	Temp. (°C.)	Space Vel.	TBHP Cv(%)	Sel. TBA	Sel. Acet.	Sel. MeOH	Sel. DTBP
6879-31-1	Pd (.08%)	80	0.5	88.9	82.8	9.7	1.9	7.5
6879-31-2	on Al ₂ O ₃	100	0.5	93.2	83.3	11.6	2.6	5.1
6879-31-3		120	0.5	96.2	81.6	13.9	3.3	4.4
6879-31-4		140	0.5	97.4	82.0	14.0	2.9	4.0
6879-32-1	Pd (.08%)	80	1.0	78.0	83.0	9.6	1.6	7.4
6879-32-2	on Al ₂ O ₃	100	1.0	88.7	80.3	14.9	3.2	4.7
6879-32-3		120	1.0	93.6	78.1	18.4	4.7	3.5
6879-32-4		140	1.0	97.0	77.0	20.4	5.9	2.7
6879-33-1	Pd (.08%)	80	2.0	45.0	82.9	7.5	1.2	9.6
6879-33-2	on Al ₂ O ₃	100	2.0	85.7	79.9	15.7	3.9	4.4
6879-33-3		120	2.0	94.5	74.8	22.5	6.9	2.7
6879-33-4		140	2.0	96.9	73.7	24.1	7.9	2.1

TABLE 11

CATALYTIC CONVERSION OF TBHP TO TBA (CONTINUOUS REACTOR)								
Notebook Number	Catalyst	Temp. (°C.)	Space Vel.	TBHP Cv (%)	Sel. TBA	Sel. Acet.	Sel. MeOH	Sel. DTBP
6906-14-1	TiO ₂	80	0.5	22.5	80.5	11.6	1.3	7.9
6906-14-2		100	0.5	72.0	79.3	16.4	3.3	4.3
6906-14-3		120	0.5	92.7	66.4	31.0	8.5	2.5
6906-14-4	TiO ₂	140	0.5	98.5	66.1	32.8	8.9	1.1
6906-15-1		80	1.0	8.3	0.0	0.0	0.0	0.0
6906-15-2		100	1.0	35.8	82.2	13.0	2.6	4.8
6906-15-3	TiO ₂	120	1.0	89.2	70.4	27.5	8.1	2.1
6906-15-4		140	1.0	99.5	59.3	40.6	10.5	0.2
6906-16-1		80	2.0	3.4	0.0	0.0	0.0	0.0
6906-16-2	TiO ₂	100	2.0	16.4	80.7	14.1	2.3	5.2
6906-16-3		120	2.0	55.1	76.9	20.0	3.5	3.0
6906-16-4		140	2.0	89.0	62.8	36.2	11.7	1.0

TABLE 12

CATALYTIC CONVERSION OF TBHP TO TBA (CONTINUOUS REACTOR)								
Notebook Number	Catalyst	Temp. (°C.)	Space Vel.	TBHP Cv(%)	Sel. TBA	Sel. Acet.	Sel. MeOH	Sel. DTBP
6906-17-1	ZrO ₂	80	0.5	19.7	81.1	10.8	1.3	8.2
6906-17-2		100	0.5	77.5	79.2	15.8	3.8	5.0
6906-17-3		120	0.5	100.0	67.5	30.2	7.8	2.3
6906-17-4	ZrO ₂	140	0.5	100.0	66.4	32.5	7.3	1.1
6906-18-1		80	1.0	7.1	0.0	0.0	0.0	0.0
6906-18-2		100	1.0	53.9	80.8	13.7	3.3	5.6
6906-18-3	ZrO ₂	120	1.0	95.9	70.9	26.8	6.8	2.3
6906-18-4		140	1.0	96.9	63.6	35.6	8.2	0.8
6906-19-1		80	2.0	4.5	0.0	0.0	0.0	0.0
6906-19-2	ZrO ₂	100	2.0	28.9	80.4	13.4	3.1	6.2
6906-19-3		120	2.0	83.0	85.8	11.6	7.0	2.6
6906-19-4		140	2.0	94.9	65.3	34.0	8.6	0.7

Having thus described our invention, what is claimed is:

1. In a method wherein a solvent solution of a tertiary butyl hydroperoxide charge stock is brought into contact with a catalytically effective amount of a hydroperoxide decomposition catalyst in a hydroperoxide decomposition reaction zone in liquid phase with agitation to convert said tertiary butyl hydroperoxide to decomposition products, principally tertiary butyl alcohol, the improvement which comprises:

a) using, as said hydroperoxide decomposition catalyst, a hydroperoxide decomposition catalyst consisting essentially of alumina having deposited thereon a mixture of palladium and gold in the ratio of about 0.01 to about 1 part of gold per part of titania or zirconia, and

b) recovering tertiary butyl alcohol from the products of said hydroperoxide decomposition reaction.

2. A method as in claim 1 wherein the solvent comprises tertiary butyl alcohol.

3. A method as in claim 1 wherein the solvent comprises a mixture of isobutane with tertiary butyl alcohol.

4. In a method wherein a solution of a tertiary butyl hydroperoxide charge stock in tertiary butyl alcohol that contains from about 5 to about 30 wt. % of tertiary butyl hydroperoxide is brought into contact with a catalytically effective amount of a hydroperoxide decomposition catalyst in a hydroperoxide decomposition reaction zone in liquid phase with agitation under hydroperoxide conversion conditions including a temperature within the range of about 25° to about 250° C. and a pressure of about 0 to about 1,000 psig to convert said tertiary butyl hydroperoxide to decomposition prod-

ucts, principally tertiary butyl alcohol, the improvement which comprises:

a) using, as said hydroperoxide decomposition catalyst, a supported hydroperoxide decomposition catalyst consisting essentially of alumina having deposited thereon from about 0.1 to about 1 wt. % of a mixture of palladium and gold in the ratio of about 0.01 to about 1 part of gold per part of palladium and a diluent consisting essentially of 100 to 500 wt. % of titania or zirconia, based on the weight of the alumina, and

b) recovering tertiary butyl alcohol from the products of said hydroperoxide decomposition reaction.

5. A method as in claim 4 wherein the temperature is in the range of about 40° to about 150° C. and the pressure is about 0 psig.

6. In a method wherein a solution of a tertiary butyl hydroperoxide charge stock in a mixture of isobutane with tertiary butyl alcohol that contains from about 5 to about 30 wt. % of tertiary butyl hydroperoxide is brought into contact with a catalytically effective amount of a hydroperoxide decomposition catalyst in a hydroperoxide decomposition reaction zone in liquid phase with agitation under hydroperoxide conversion conditions including a temperature within the range of about 25° to about 250° C. and a pressure of about 0 to about 1,000 psig to convert said tertiary butyl hydroperoxide to decomposition products, principally tertiary butyl alcohol, the improvement which comprises:

a) using, as said hydroperoxide decomposition catalyst, a diluted hydroperoxide decomposition catalyst consisting essentially of alumina having deposited thereon from about 0.1 to about 1 wt. % of a mixture of palladium and gold in the ratio of about

17

0.01 to about 1 part of gold per part of palladium, and a diluent consisting essentially of about 100 to about 500 wt. % of zirconia, based on the hydroperoxide decomposition catalyst,

18

b) recovering tertiary butyl alcohol from the products of said hydroperoxide decomposition reaction.
7. A method as in claim 6 wherein the temperature is in the range of about 40° to about 150° C. and the pressure is about 0 psig.

* * * * *

10

15

20

25

30

35

40

45

50

55

60

65